# PROCESS FOR UPGRADING FCC PRODUCT WITH ADDITIONAL REACTOR

## BACKGROUND OF THE INVENTION

[0001]    This invention relates generally to processes for the fluidized catalytic

cracking (FCC) of heavy hydrocarbon streams. More specifically, this invention relates

generally to processes for upgrading catalytically cracked hydrocarbon feeds in a

discrete reactor vessel.

## DESCRIPTION OF THE PRIOR ART

[0002]    The FCC process is carried out by contacting the starting material whether it

be vacuum gas oil, reduced crude, or another source of relatively high boiling

hydrocarbons with a catalyst made up of finely divided or particulate solid material.

The catalyst is transported in a fluid-like manner by passing gas or vapor through it at

sufficient velocity to produce a desired regime of fluid transport. Contact of the oil

with the fluidized material catalyzes the cracking reaction. The cracking reaction

deposits coke on the catalyst. Coke is comprised of hydrogen and carbon and can

include other materials in trace quantities such as sulfur and metals that enter the

process with the starting material. Coke interferes with the catalytic activity of the

106287                                    - 1 -

catalyst by blocking active sites on the catalyst surface where the cracking reactions take place. Catalyst is traditionally transferred from a stripper, that removes adsorbed hydrocarbons and gases from catalyst, to a regenerator for purposes of removing the coke by oxidation with an oxygen-containing gas. An inventory of catalyst having a

5       reduced coke content, relative to the catalyst in the stripper, hereinafter referred to as regenerated catalyst, is collected for return to the reaction zone. Oxidizing the coke from the catalyst surface releases a large amount of heat, a portion of which escapes the regenerator with gaseous products of coke oxidation generally referred to as flue gas. The balance of the heat leaves the regenerator with the regenerated catalyst. The

10      fluidized catalyst is continuously circulated from the reaction zone to the regeneration zone and then again to the reaction zone. The fluidized catalyst, as well as providing a catalytic function, acts as a vehicle for the transfer of heat from zone to zone. Catalyst exiting the reaction zone is spoken of as being spent, i.e., partially deactivated by the deposition of coke upon the catalyst. The FCC processes, as well as separation devices

15      used therein are fully described in US 5,584,985 B1 and US 4,792,437 B1, the contents of which are hereby incorporated by reference. Specific details of the various contact zones, regeneration zones, and stripping zones along with arrangements for conveying the catalyst between the various zones are well known to those skilled in the art.

20      [0003]    The FCC reactor cracks gas oil or heavier feeds into a broad range of products. Cracked vapors from the FCC unit enter a separation zone, typically in the

106287                                      - 2 -

form of a main column, that provides a gas stream, a gasoline cut, light cycle oil

(LCO) and clarified oil (CO) which includes heavy cycle oil (HCO) components. The

gasoline cut may include light, medium and heavy gasoline components. A major

component of the heavy gasoline fraction comprises condensed single ring aromatics. A

5       major component of LCO is condensed bicyclic ring aromatics.

[0004]    Subjecting product fractions to additional reactions is useful for upgrading

product quality. The recracking of heavy product fractions from the initially cracked

FCC product is one example. Typically, in recracking, uncracked effluent from a first

riser of an FCC reactor is recontacted with catalyst at a second location to cleave larger

10      molecules down into more useful smaller molecules. For example, US 4,051,013 B1

discloses cracking both gasoline-range feed and gas oil feed in the same riser at

different elevations. US 3,161,582 B1, US 5,176,815 B1 and US 5,310,477 B1 all

disclose cracking a primary hydrocarbon feed in a riser of an FCC unit and cracking a

secondary hydrocarbon feed in a reactor into which the riser exits. As a result, both

15      cracked products mix in the reactor, to some extent, which could negate the

incremental upgrade resulting from cracking the secondary hydrocarbon feed,

particularly if it is a fraction of the cracked primary hydrocarbon feed.

[0005]    FCC units employing two risers are known. US 5,198,590 B1, US

4,402,913 B1, US 4,310,489 B1, US 4,297,203 B1, US 3,799,864 B1, US 3,748,251

20      B1, US 3,714,024 B1 and WO 00/40672 disclose two riser FCC units in which feeds

are predominantly cracked in both risers. In these patents, both risers communicate

106287                                          - 3 -

with the same recovery conduit and/or reactor permitting commingling of gaseous

products. In US 5,730,859 B1, all of the effluent from one riser is fed to the other

riser, without first undergoing a product separation. US 4,172,812 B1 teaches

recracking all or a part of cracked product from a riser of an FCC unit over a catalyst

5      having a composition that is different from the catalyst composition in the riser.

[0006]     In US 5,944,982 B1, although both risers terminate in the same reactor

vessel, gaseous products from each riser are isolated from the other. This patent also

discusses the method of cracking a LCO fraction of a cracked product containing very

refractory, bicyclic aromatic components. Bicyclic aromatics are very difficult to crack

10     and boil only at high temperatures. The presence of high boiling point bicyclic

aromatics can cause a gasoline pool to exceed maximum volatility standards. By a

process called J-cracking, LCO is hydrotreated to partially saturate the bicyclic

aromatic hydrocarbons such as naphthalene to produce tetralin. The tetralin is then

cracked to make benzene, toluene, xylene and isoparaffins along with some

15     naphthalene. The "J" in J-cracking is a measure of unsaturation of the hydrocarbons

having the general formula:

$$C_NH_{2N-J}.$$

[0007]     US 3,928,172 B1 teaches an FCC unit with a secondary dense fluidized

catalyst bed in a separate reactor. Gas oil is cracked in a riser of the FCC unit with

20     unregenerated catalyst from the separate dense fluidized catalyst bed. A heavy naphtha

fraction of the cracked gas oil, boiling between 127° and 232°C (260° and 450°F),

from the riser is recracked in the separate reactor over regenerated catalyst. Apparently, the benefit of cracking lower boiling fractions was not explored, presumably because the octane rating of the lower boiling fraction was sufficiently high or because it was predicted not to be effective. The data in the patent indicates that nominal, if any, reformulation reactions occur in the separate reactor because little, if any, new aromatics are produced.

[0008]    It is also known to subject cracked product from a riser of an FCC unit to a subsequent oligomerization reaction in a separate reactor. In oligomerization, smaller olefins are bonded together to make larger olefins of greater molecular weight. US 5,009,851 B1 and US 4,865,718 B1 disclose oligomerizing a fraction of cracked product from an FCC unit in a separate reactor.

[0009]    Cracking and oligomerization differ from reformulation in that the former involve decreases or increases in carbon numbers, respectively. Whereas, in reformulation, carbon numbers are not changed but hydrogen atoms are exchanged to alter the structure of the molecule and make it more valuable.

[0010]    In gasoline production, many governmental entities are restricting the concentration of olefins allowed in the gasoline pool. Reducing olefin concentration without also reducing value is difficult because higher olefin concentrations typically promote higher Research Octane Numbers (RON) and Motor Octane Numbers (MON), but the latter to a lesser extent. Octane value or Road Octane Number is the average of RON and MON. Merely saturating olefins typically yields normal paraffins which

typically have low octane value. Additionally, saturation requires the addition of hydrogen, which is expensive and in some regions, difficult to obtain.

[0011]    Feedstocks for FCC units typically include sulfur and nitrogen. During FCC operation, the sulfur and nitrogen are converted primarily to hydrogen sulfide and ammonia, which are easily removed, but are also converted to organic sulfurs, mercaptans and nitrogen oxides. Stricter environmental limits on sulfur and nitrogen compound emissions along with lower sulfur specifications for fuel products have raised interest in the need to remove nitrogen and sulfur compounds from FCC gasoline. As demands for cleaner fuels and use of high sulfur and high nitrogen feedstocks increase, the need for sulfur and nitrogen removal from FCC gasoline will become even greater.

[0012]    It is an object of the present invention to provide a method for enhancing the quality of product from an FCC unit. It is a further object of the present invention to reduce the olefinicity of product from an FCC unit without substantially reducing the octane rating of the product and without the addition of hydrogen. It is an even further object of the present invention to reduce the concentration of sulfur and nitrogen compounds in an FCC product.

## BRIEF SUMMARY OF THE INVENTION

[0013]    It has now been discovered that a separate reactor can be used to either reformulate or crack a product fraction from an FCC unit to reduce its olefinicity and

maintain or boost its octane rating without the separate addition of hydrogen. If the

separate reactor is incorporated into an FCC unit, catalyst can be circulated between

the FCC reactor and the separate reactor. Additionally, it has been further found that

higher boiling point fractions from an FCC unit can be hydrotreated and sent to a

5    separate reactor, if incorporated in the FCC unit using catalyst cycled through the FCC

unit, to crack FCC product fractions down to lower boiling point useful hydrocarbon

components. Furthermore, reacting fractions of FCC product in a separate reactor has

been found effective in substantially reducing sulfur and nitrogen compounds in the

fraction.

10   [0014]    Accordingly, in one embodiment, the present invention relates to a process

for converting a hydrocarbon feed stream comprising passing a reformulation feed

stream including saturated and olefinic hydrocarbons with carbon numbers of 5-8 to a

reformulating reactor. The reformulating reactor contains catalyst particles having a

composition. The reformulation feed stream is reformulated in the reformulating

15   reactor to produce a reformulated product stream. The reformulating proceeds at

conditions that promote at least a 5% net yield increase in aromatics on a fresh

reformulation feed basis indicating the occurrence of hydrogen transfer reactions. The

reformulated product stream is then recovered.

[0015]    In another embodiment, the present invention relates to a process for

20   converting a hydrocarbon feed stream comprising contacting the hydrocarbon feed

stream with catalyst particles having a composition in a first reactor to produce a

106287                                      - 7 -

cracked product. The cracked product is separated from the catalyst particles in a

vessel to obtain a cracked product stream. A naphtha stream is recovered from the

cracked product stream. The naphtha stream has an initial boiling point below 127°C

(260°F). The naphtha stream is contacted with catalyst particles having the composition

5      in a second reactor to produce an upgraded product stream. The upgraded product

stream is recovered and isolated from the cracked product stream.

[0016]      In a further embodiment, the present invention relates to a process for

converting a hydrocarbon feed stream comprising contacting the hydrocarbon feed

stream with catalyst particles having a composition in a first reactor to produce a

10      cracked product. The cracked product is separated from the catalyst particles in a

vessel to obtain a cracked product stream. An oil stream is recovered from the cracked

product stream having an initial boiling point above about 200°C (392°F). Catalyst

particles that had resided in the first reactor are cycled to a second reactor that is

discrete from the vessel. The oil stream is contacted with catalyst particles in a second

15      reactor to produce an upgraded product stream. The upgraded product stream is

recovered and isolated from the cracked product stream.

[0017]      Additional objects, embodiment and details of this invention can be obtained

from the following detailed description of the invention.

106287                                    - 8 -

# BRIEF DESCRIPTION OF THE DRAWINGS

[0018]    FIG. 1 is a sectional, elevational, schematical view of an FCC unit incorporating a main column and a secondary reactor in accordance with the present invention.

[0019]    FIG. 2 is a sectional, elevational, schematical view of an alternative embodiment of the present invention.

[0020]    FIG. 3 is a sectional, elevational, schematical view of a further embodiment of the present invention.

# DETAILED DESCRIPTION OF THE INVENTION

[0021]    The present invention may be described with reference to four components: an FCC reactor 10, a regenerator 50, a secondary reactor 80, 80', 80" and a main column 100. Although many configurations of the present invention are possible, three specific embodiments are presented herein by way of example. All other possible embodiments for carrying out the present invention are considered within the scope of the present invention. For example, the secondary reactor 80, 80', 80" and/or the main column 100 need not be incorporated into an FCC unit as illustrated in FIGS. 1-3 but may stand alone.

[0022]    In the embodiment of the present invention in FIG. 1, the FCC reactor 10 comprises a conduit in the form of a reactor riser 12 that extends upwardly through a lower portion of a reactor vessel 14 as in a typical FCC arrangement. The central

conduit or reactor riser 12 preferably has a vertical orientation within the reactor vessel

14 and may extend upwardly through the bottom of the reactor vessel 14 or

downwardly from the top of the reactor vessel 14. The reactor riser 12 terminates in a

separation vessel 16 at swirl arms 18. A hydrocarbon feed stream is fed to the riser at a

5     nozzle 20 which is contacted and vaporized by hot regenerated catalyst fluidized by a

gas such as steam from a nozzle 22. The catalyst cracks the hydrocarbon feed stream

and a mixture of catalyst particles and gaseous cracked hydrocarbons exit the swirl

arms 18 into the separation vessel 16. Tangential discharge of gases and catalyst from

the swirl arms 18 produces a swirling helical motion about the interior of the separation

10    vessel 16, causing heavier catalyst particles to fall into a dense catalyst bed 24 and a

mixture of gaseous cracked hydrocarbons and entrained catalyst particles to travel up a

gas recovery conduit 26 and enter into cyclones 28. In the cyclones 28, centripetal

force imparted to the mixture induces the heavier entrained catalyst particles to fall

through diplegs 30 of the cyclone 28 and to the bottom of the separation vessel 16 into

15    a dense catalyst bed 32. The gases in the cyclones 28 more easily change direction and

begin an upward spiral with the gases ultimately exiting the cyclones 28 through outlet

pipes 34. Cracked gases leave the reactor vessel 14 though an outlet conduit 36. The

cracked gases are optionally subjected to a further separation (not shown) to further

remove any light loading of catalyst particles and are sent via a line 98 to fractionation

20    in the main column 100 which will be described later with reference to all of FIGS.

1-3. Catalyst particles in the dense catalyst bed 32 enter the separation vessel 16

through windows 38 where they join catalyst particles in the dense catalyst bed 24 in a stripping section 40 of the separation vessel 16. The catalyst particles are stripped of entrained cracked vapors over baffles 42 with a stripping medium such as steam entering from at least one nozzle 44. The stripped cracked vapors travel up to the gas

5    recovery conduit 26 where they are processed with other cracked product vapors.

[0023]    Stripped catalyst from the stripping section 40 of the FCC reactor 10 travels through a first stripped catalyst pipe 46 regulated by a control valve 48 and into the regenerator 50 at a lower chamber 52. In the lower chamber 52, stripped catalyst is subjected to hot oxygen-containing gas such as air from a distributor 54. Coke is

10    burned from the catalyst and as the catalyst is heated, it ascends upwardly in the lower chamber 52 and is distributed into an upper chamber 55 of the regenerator through a distributor 56. Regenerated catalyst collects in a dense catalyst bed 58 whereas entrained catalyst is removed from regenerator effluent gases in cyclones 60 and 62. Flue gas exits the cyclone 62 through an outlet pipe 64 to exit the regenerator through

15    an outlet 66. Regenerated catalyst from the dense catalyst bed 58 travels through a regenerated catalyst pipe 68 regulated by a control valve 70 into the reactor riser 12 where it is fluidized and contacted with fresh feed. Stripped catalyst also exits the stripping section 40 through a second stripped catalyst pipe 72 regulated by a control valve 74 into a dense catalyst bed 82 in the secondary reactor 80. The degree to which

20    the control valve 74 is opened can be automatically controlled to obtain the temperature desired in the secondary reactor 80. For example, if higher temperature is desired in

the secondary reactor 80, more of the relatively hot catalyst can be permitted to pass

through the control valve 74 to add heat to the secondary reactor 80. The secondary

reactor 80 is preferably a fluidized bed. However, a riser reactor or other reactor

configuration may be suitable. A partition defines a hopper section 81 of the secondary

reactor 80. Catalyst in the dense catalyst bed 82 that falls into the hopper section 81 is

fluidized by steam or some other fluidizing media through a distributor 84 and is

stripped of entrained gases over baffles 83. A desired cut of hydrocarbon feed from the

FCC reactor 10 and fractionated in the main column 100 is fed to a secondary reactor

80. The feed to the secondary reactor 80 from the main column 100 is fed through a

distributor 86 where it is contacted with catalyst in the dense catalyst bed 82. The

distributor 86 distributes feed in such a way as to fluidize the dense catalyst bed 82.

Cyclones 88 and 90 remove entrained catalyst from a gaseous product which leaves the

secondary reactor 80 through a conduit 92. Catalyst leaves the secondary reactor 80

after being stripped in the hopper section 81 through a pipe 76 regulated by a control

valve 78. The degree to which the control valve 78 is opened can be automatically

controlled to obtain the level desired in the secondary reactor 80. The level of the

catalyst in the secondary reactor 80 determines the weight hourly space velocity

(WHSV) of reactants through the secondary reactor 80. For example, if a greater

WHSV is desired, the control valve 78 would be opened relatively more to reduce the

level of catalyst in the dense catalyst bed 82.

[0024]    FIG. 2 is an alternative embodiment of the present invention in which regenerated catalyst is fed to the secondary reactor 80'. In FIG. 2, the elements of the FCC reactor 10 and the regenerator 50 have generally the same configuration as in FIG. 1. Elements in FIG. 2 with different configurations from FIG. 1, such as in the secondary reactor 80', will be distinguished by adding a " ' " symbol to the reference numeral. Hydrocarbon feed processed in the FCC reactor 10 is recovered at the outlet conduit 36 and is carried by the line 98 to be fractionated in the main column 100, perhaps after interim processing, to obtain a desired cut to be fed to the secondary reactor 80'. The feed to the secondary reactor 80' is fed by a fluidizing nozzle 85 to be contacted in a riser 86' with regenerated catalyst from a regenerated catalyst pipe 68' regulated by a control valve 70'. Both feed and catalyst are distributed by the riser 86' into a dense catalyst bed 82' which is fluidized by the feed from the riser 86'. Products exit the secondary reactor 80' out a conduit 92' after entrained catalyst is removed in cyclones 88' and 90'. A partition defines a hopper section 81' of the secondary reactor 80'. Catalyst from the dense catalyst bed 82' in the secondary reactor 80' that falls into the hopper section 81' is fluidized with a medium such as steam from a distributor 84' and is stripped of entrained product gases over baffles 83'. Stripped catalyst passes through a pipe 76' regulated by a control valve 78' to the reactor riser 12 where it contacts the primary hydrocarbon feed stream injected by the nozzle 20. Stripped catalyst from the stripping section 40 of the FCC reactor 10 passes through a stripped catalyst pipe 46' regulated by a control valve 48' into the lower chamber 52 of the

regenerator 50 where coke deposits are burned from catalyst by means of a hot oxygen-containing gas such as air. Regenerated catalyst from the upper chamber 55 passes through the regenerated catalyst pipe 68' and is regulated by the control valve 70' before it enters the riser 86' of the secondary reactor 80'. All other elements in FIG. 2 have generally the same function as in FIG. 1.

[0025]     FIG. 3 shows another embodiment of an FCC unit utilizing a secondary reactor 80" which receives catalyst from and returns catalyst to the regenerator 50. Again, because the FCC reactor 10 and the regenerator 50 are both very similar to those depicted in FIG. 1, all of their elements in both drawings will retain the same reference numerals. However, those elements in FIG. 3 that differ from the corresponding elements in FIG. 1 will be distinguished by adding a " " " symbol to the reference numeral. Primary hydrocarbon feed is fed to the reactor riser 12 by means of the nozzle 20. The primary feed is contacted with regenerated catalyst and cracked to yield product that is withdrawn from the FCC reactor 10 via the outlet conduit 36. Catalyst separated from the cracked product is stripped in the stripping section 40 and passed through a stripped catalyst pipe 46" regulated by a control valve 48" into the lower chamber 52 of the regenerator 50. Regenerated catalyst from the upper chamber 55 of the regenerator 50 is distributed to the reactor riser 12 through a first regenerated catalyst pipe 68" regulated by a control valve 70" where it contacts fresh primary feed and is also distributed through a second regenerated catalyst pipe 72" regulated by a control valve 74" to the secondary reactor 80". The gaseous vapor effluent from the

FCC reactor 10 is carried from the outlet conduit 36 through the line 98, perhaps to further processing and then to the main column 100 to be fractionated. A desired fraction is fed to the secondary reactor 80" through a distributor 86" which fluidizes a dense catalyst bed 82" with a medium such as steam. The feed contacts regenerated catalyst in the dense catalyst bed 82". A partition defines a hopper section 81" in the secondary reactor 80". Catalyst from the dense catalyst bed 82" of the secondary reactor 80" that falls into the hopper section 81" is fluidized by steam of some other fluidizing media through a distributor 84" and is stripped of entrained gases over baffles 83". Stripped catalyst passes through a pipe 76" regulated by a control valve 78" to the regenerator 50. The product from the secondary reaction is recovered through cyclones 88" and 90" which remove entrained catalyst and send the catalyst back to the dense catalyst bed 82". A conduit 92" carries gaseous product to further processing which could consist of heating and fractionating.

[0026]    The secondary reactor 80, 80', 80" may stand alone instead of being incorporated into an FCC unit. If the secondary reactor 80, 80', 80" stands alone, the preferred feed will be a cut of product from an FCC unit.

[0027]    In reference to all of FIGS. 1-3, the cracked product stream in the line 98 from the FCC reactor 10, relatively free of catalyst particles and including the stripping fluid, exits the reactor vessel 14 through the outlet conduit 36. The cracked product stream in the line 98 may be subjected to additional treatment to remove fine catalyst particles or to further prepare the stream prior to fractionation. The line 98 transfers

the product stream containing the cracked product to a fractionator in the form of the main column 100. A variety of products are withdrawn from the main column 100. In this case, the main column 100 recovers an overhead stream of light products comprising unstabilized gasoline and lighter gases. A line 102 transfers the overhead stream through a condenser 104 and a cooler 106 before it enters a receiver 108. A line 110 withdraws a light off-gas stream from the receiver 108. A bottom liquid stream of light gasoline leaves the receiver 108 via a line 112 which may have to undergo further treatment to stabilize the light gasoline. The main column 100 also provides a heavy gasoline stream, an LCO stream and an HCO stream through lines 120, 122 and 124, respectively. Parts of the streams in the lines 120, 122 and 124 are all circulated through heat exchangers 126, 128 and 130 and reflux loops 132, 134 and 136, respectively, to remove heat from the main column 100. Streams of heavy gasoline, LCO and HCO are transported from the main column 100 through respective lines 140, 142 and 144. A CO fraction may be recovered from the bottom of the main column 100 via a line 146. Part of the CO fraction is recycled through a reboiler 148 and returned to the main column 100 through a line 150. The CO stream is removed from the main column 100 via a line 152.

[0028]    The light gasoline or light naphtha fraction preferably has an initial boiling point (IBP) below 127°C (260°F) in the $C_5$ range; i.e., about 35°C (95°F), and an end point (EP) at a temperature greater than or equal to 127°C (260°F). The boiling points for these fractions are determined using the procedure known as ASTM D86-82. The

heavy gasoline or heavy naphtha fraction has an IBP at or above 127°C (260°F) and an

EP at a temperature above 200°C (392°F), preferably between 204° and 221°C (400°

and 430°F), particularly at 216°C (420°F). The LCO stream has an IBP at about the

EP temperature of the heavy gasoline and an EP in a range of 260° to 371°C (500° to

5      700°F) and preferably 288°C (550°F). The HCO stream has an IBP of the EP

temperature of the LCO stream and an EP in a range of 371° to 427°C (700° to

800°F), and preferably about 399°C (750°F). The CO stream has an IBP of the EP

temperature of the HCO stream and includes everything boiling at a higher

temperature. One or more of each of these streams or other cuts from the main column

10     100 are sent to the secondary reactor 80, 80', 80" to be contacted with the catalyst

therein. In one embodiment, a stream such as the line 142 which carries LCO may be

hydrotreated in a hydrotreating reactor 154 before it is sent to the secondary reactor

80, 80', 80" for cracking. Other streams from the main column 100 could be

hydrotreated before entering the secondary reactor 80, 80', 80".

15     **[0029]**      In the secondary reactor 80, 80', 80", the predominant reaction may be

cracking in which a hydrocarbon molecule is broken into two smaller hydrocarbon

molecules, so that the number of carbon atoms in each molecule diminishes.

Alternatively, the predominant reaction in the secondary reactor 80, 80', 80" may be a

hydrogen-transfer reaction such as reformulation or isomerization in which the

20     structures of the molecules are changed but the number of carbon atoms in each

molecule does not change. In determining which type of reaction, cracking or hydrogen

transfer, predominates over the other, reactions involving compounds with 5 to 8

carbons may be the most relevant because they include most of the olefins which can

either crack or reform.

[0030]    Olefins, naphthenes and cyclo-olefins are reformulated into paraffins,

aromatics and some naphthenes as shown in formulas (1), (2), (3) and (4).

$$3\,C_n\,H_{2n} + C_m\,H_{2m} \rightarrow 3\,C_n\,H_{2n+2} + C_m\,H_{2m-6} \qquad (1)$$
$$\text{olefins} + \text{naphthene} \rightarrow \text{paraffins} + \text{aromatic}$$

$$4\,C_n\,H_{2n} \rightarrow 3\,C_n\,H_{2n+2} + C_n\,H_{2n-6} \qquad (2)$$
$$\text{olefins} \rightarrow \text{paraffins} + \text{aromatic}$$

$$C_m\,H_{2m-2} + 2\,C_n\,H_{2n} \rightarrow C_m\,H_{2m-6} + 2\,C_n\,H_{2n+2} \qquad (3)$$
$$\text{cyclo-olefins} + \text{olefins} \rightarrow \text{aromatic} + \text{paraffins}$$

$$C_n\,H_{2n} + H_2 \rightarrow C_n\,H_{2n+2} \qquad (4)$$
$$\text{olefins} + \text{hydrogen} \rightarrow \text{paraffins}$$

Olefins have a higher octane value than their paraffinic counterpart. Hence, the

conversion of olefins to paraffins typically degrades octane value. When the olefins

cyclitize to become aromatics as shown in formulas (1) and (2) and when cyclo-olefins

aromaticize to yield aromatics as in formula (3), they donate much hydrogen. Other

olefins pick up the hydrogen to become paraffins as shown in formula (4). In the

present invention using the secondary reactor 80, 80', 80", normal olefins and iso-

olefins predominantly reformulate to isoparaffins which carry a higher octane rating

than normal paraffins. Additionally, aromatics also boost the octane rating of the

product. Because the isoparaffins and aromatics have a high octane rating, the hydrogen transfer reformulation in the secondary reactor 80, 80', 80" maintains the high octane ratings despite the typical octane rating decline that accompanies conversion of olefins to paraffins. Accordingly, the hydrogen-transfer reactions in the

5      secondary reactor 80, 80', 80" which yield more isoparaffins and aromatics are superior to a process which saturates the olefins into normal paraffins. Advantageously, the hydrogen transfer reactions are performed without the addition of hydrogen, which can be expensive and difficult to obtain.

[0031]     Production of aromatics is a gauge for the degree of hydrogen transfer that

10     occurs in the reaction. When conditions are set to promote hydrogen transfer reactions in the secondary reactor 80, 80', 80", a net yield increase in aromatics of 5% on a fresh feed basis is typical and at least a 40% increase is easily attainable.

[0032]     The reaction in the secondary reactor 80, 80', 80" is preferably conducted with the same catalyst circulated through the regenerator 50 and the FCC reactor 10.

15     Of course, if a secondary reactor 80, 80', 80" stands alone without incorporation into an FCC unit, the catalyst in the secondary reactor need not be circulated through an FCC unit. If hydrogen-transfer reactions are intended to predominate over cracking reactions in the secondary reactor, the WHSV will typically range from 0.1 to 5 $hr^{-1}$. If cracking reactions are to predominate over hydrogen-transfer reactions, the WHSV

20     will typically range from 5 to 50 $hr^{-1}$. Additionally, the conditions in a hydrogen-transfer reaction are less severe, with temperatures in the range of 399° to 510°C

106287                                         - 19 -

(750° to 950°F) than in a cracking reaction with temperatures in the range of 482° to 649°C (900° to 1200°F).

[0033]     An additional advantage of the hydrogen transfer reaction in the secondary reactor 80, 80', 80" is that it is endothermic. Hence, the spent catalyst which contacts the hydrocarbon stream in the dense catalyst bed 82, 182, 282 is cooled before it is sent back to the reactor riser 12 of the FCC reactor 10 or the regenerator 50. Consequently, heat will be removed from the whole system which permits use of a greater catalyst-to-oil ratio in the reactor riser 12, resulting in higher conversion in the FCC reactor 10.

[0034]     The reformulation of the fraction from the main column 100 by hydrogen transfer in the secondary reactor 80, 80', 80" reduces the concentrations of organic sulfur and nitrogen compounds in the products. The reaction of the gasoline fraction in the secondary reactor 80, 80', 80" can lower sulfur concentration in the reactor products by as much as 80 wt-% and nitrogen concentration in the products by as much as 98 wt-%. Hence, the products from the secondary reactor 80, 80', 80" will contain low concentrations of sulfur and nitrogen compounds. Leftover sulfur and nitrogen compounds can be removed from the product by hydrotreating and taken off in the overhead of a finishing distillation column if necessary to meet specifications.

[0035]     Typically, the catalyst circulation rate through the reactor riser 12 and the input of feed and any lift gas that enters the riser will produce a flowing density of between 48 and 320 kg/m$^3$ (3 and 20 lbs/ft$^3$) and an average velocity of about 3 to 31 m/sec (10 to 100 ft/sec) for the catalyst and gaseous mixture. In the FCC reactor 10,

catalyst will usually contact the hydrocarbons in a catalyst to oil ratio in a range of

from 3 to 8, and more preferably in a range of from 4 to 6. The length of the reactor

riser 12 will usually be set to provide a residence time of between 0.5 to 10 seconds at

these average flow velocity conditions. Other reaction conditions in the reactor riser 12

5    usually include a temperature of from 468° to 566°C (875° to 1050°F).

[0036]    This invention can employ a wide range of commonly used FCC catalysts.

These catalyst compositions include high activity crystalline alumina silicate or zeolite

containing catalysts. Zeolite catalysts are preferred because of their higher intrinsic

activity and their higher resistance to the deactivating effects of high temperature

10    exposure to steam and exposure to the metals contained in most feedstocks. Zeolites are

usually dispersed in a porous inorganic carrier material such as silica, aluminum, or

zirconium. These catalyst compositions may have a zeolite content of 30% or more.

Zeolites including high silica-to-alumina compositions such as LZ-210 and ZSM-5 type

materials are preferred when lighter products are desired. Another particularly useful

15    type of FCC catalysts comprises silicon substituted aluminas. As disclosed in US

5,080,778 B1, the zeolite or silicon enhanced alumina catalysts compositions may

include intercalated clays, also generally known as pillared clays. The preferred

catalysts for the present invention include USY zeolites. When hydrogen-transfer

reactions are desired to predominate over cracking reactions in the secondary reactor

20    80, 80', 80", high rare earth content Y zeolites are preferred. The term "high rare

earth content" denotes greater than about 2.0 wt-% rare earth oxide on the zeolite

portion of the catalyst. High rare earth content Y zeolites such as USY zeolite may have as much as 4 wt-% rare earth. The high rare earth content promotes hydrogen transfer by increasing adjacent acid site density on the catalyst. Strongly acidic catalyst sites on the catalyst promote cracking. Y zeolites with low rare earth content can still

5 effectively promote hydrogen transfer but with longer reactor residence times. When cracking reactions are desired to predominate over hydrogen transfer reactions in the secondary reactor 80, 80', 80", low rare earth Y zeolite catalysts are preferred which have a rare earth oxide content of 2.0 wt-% or less. Additives, such as sulfur-reducing additives, may be added to the catalyst. It is anticipated that such additives may

10 experience enhanced effectiveness in the secondary reactor for longer residence times.

[0037]     Feeds suitable for processing by this invention include conventional FCC feedstocks or higher boiling hydrocarbon feeds. The most common of the conventional feedstocks is a vacuum gas oil which is typically a hydrocarbon material having a boiling range of from 343° to 552°C (650° to 1025°F) and is prepared by vacuum

15 fractionation of atmospheric residue. Such fractions are generally low in coke precursors and heavy metals which can deactivate the catalyst.

[0038]     When LCO is the feed to the secondary reactor 80, 80', 80", a portion of the LCO fraction will typically pass through the hydrotreating reactor 154 and be transported through a line 156 to the secondary reactor 80, 80', 80" in which

20 J-cracking occurs. When operating in the LCO mode of this invention, the LCO cut carries bicyclic aromatic compounds into the secondary reactor 80, 80', 80" which

cannot be cracked unless they are pretreated. These bicyclic compounds include

indenes, biphenyls and naphthalenes which are refractory to cracking under the

conditions in the reactor riser 12. In the J-cracking process, one of the rings of the

bicyclic hydrocarbons are saturated. The saturated ring is then cracked in the secondary

5    reactor 80, 80', 80" and cleaved from the aromatic ring as shown in exemplary

formulas (5) and (6).



[0039]    In formula (5), one of the rings of dimethyl naphthalene is saturated to make

dimethyl tetrahydronaphthalenes. In formula (6), the saturated ring of two dimethyl

10    tetrahydronaphthalenes are cracked and accept hydrogen donated from a ring of another

dimethyl tetrahydronaphthalene that aromaticizes. The cracked rings yield toluene and

isobutane.

[0040]    Suitable methods for carrying out J-cracking are further described in US

3,479,279 B1 and US 3,356,609 B1 which are incorporated herein by reference. The

J-cracking process eliminates about two-thirds of the high boiling aromatics from an

LCO cut bringing the effluent from the secondary reactor 80, 80', 80" into the gasoline

5    boiling range. The LCO fraction can pass through the hydrotreating reactor 154 as a

separate stream or together with another fraction from the main column 100.

[0041]    The hydrotreatment of the fraction in the hydrotreating reactor 154 takes

place at low severity conditions to avoid the saturation of the single ring aromatic

compounds in the gasoline fraction. In the method of this invention, up to 100% of the

10    fraction may be hydrotreated. Hydrotreating is carried out in the presence of a nickel-

molybdenum or cobalt-molybdenum catalyst and relatively mild hydrotreating

conditions including a temperature of 316° to 371°C (600° to 700°F), a liquid hourly

space velocity (LHSV) of from 0.2 to 2 $hr^{-1}$ and a pressure of 3447 to 10342 kPa (500

to 1500 psig).

15    [0042]    The present invention can be operated in several ways, four of which are

explained herein. In the first exemplary operation, higher proportions of LCO and LPG

are obtained. The FCC reactor 10 is run at relatively low severity with a temperature

between 482° and 521°C (900° and 970°F) and a short contact time of 1 to 3 seconds.

The FCC reactor 10 will thus operate at low conversion to yield a high proportion of

20    LCO, HCO and CO, some gasoline and some liquefied petroleum gas (LPG), all

withdrawn from the main column 100. If the feed to the FCC reactor 10 is highly

paraffinic, all of the CO can be fed to the secondary reactor 80, 80', 80". However, if

the feed is not highly paraffinic, only the HCO fraction should be fed to the secondary

reactor. Fractions of LCO and LPG product can be recovered from the main column

100. If gasoline is desired, it can be recovered from the main column and sent to the

gasoline pool. If gasoline is not desired, it can be sent with CO and HCO or alone to

the secondary reactor 80, 80', 80" which cracks the CO and HCO mixture at high

severity temperatures such as 521° to 560°C (970° to 1040°F) and preferably 549°C

(1020°F) and at a space time of 1 to 10 hr$^{-1}$. LPG and LCO are then recovered from

the secondary reactor which can be added to the fractions of LCO and LPG recovered

from the main column 100. A medium or smaller pore, shape selective zeolite additive

such as ZSM-5 may be added to the catalyst to obtain greater yields of LPG in this

operation. Because the secondary reactor is operated at high severity, FIGS. 2 or 3

would be most appropriate for this operation because the hotter catalyst from the

regenerator 50 can provide the necessary heat requirements.

[0043]     A second operation in which the present invention can be used to produce

gasoline, LPG and benzene, toluene and xylene (BTX) gasoline. The FCC reactor 10 is

run at a high severity temperature ranging from 521° to 560°C (970° to 1040°F),

preferably 549°C (1020°F) and a contact time of over 3 seconds. The high severity

cracking operation gives a high conversion with gasoline, LPG, LCO and CO in the

product stream. Gasoline and LPG are recovered from the main column 100 while

LCO is fed from the main column 100 to the hydrotreating reactor 154 to saturate one

106287                                              - 25 -

of the bicyclic aromatic rings to prepare it for cracking. The hydrotreated LCO is then sent to the secondary reactor 80, 80', 80" operated at high severity temperatures of 521° to 560°C (970° to 1040°F) sufficient to J-crack it to obtain BTX gasoline which can be mixed with gasoline to upgrade gasoline product quality. The embodiments in

5　FIGS. 2 or 3 can be used for this exemplary operation.

[0044]　In a third exemplary operation, the desired product yields up to an 80% reduction in gasoline sulfur and nitrogen and possesses an olefin concentration as low as 1 wt-%. The primary reactor is run at a severity appropriate to obtain the desired conversion. Either a full range cut of gasoline having an IBP below 127°C (260°F) and

10　an EP at or below 200°C (392°F) or a fraction thereof from the main column 100 is fed to the secondary reactor 80, 80', 80" which is run at 482° to 521°C (900° to 970°F). In the secondary reactor, the olefins reformulate via hydrogen transfer to isoparaffins and aromatics with minimal gasoline yield loss and an octane gain and without need of additional hydrogen. Moreover, sulfur levels are reduced by as much

15　as 80 wt-% and nitrogen levels are reduced by as much as 98 wt-%. If necessary, the gasoline can then be hydrotreated to reduce sulfur and nitrogen compounds to even lower levels to meet specifications by converting them to hydrogen sulfide and ammonia, respectively, which can be removed in the light ends of a downstream gasoline fractionation unit (not shown) with minimal octane debit and consumption of

20　hydrogen. This operation can be performed with any of the three embodiments in FIGS. 1-3 of the present invention.

[0045]    When the desired products are LCO and low olefinicity, moderate octane gasoline, a fourth exemplary operation may be used. The FCC reactor 10 is run at low severity at a temperature of 482° to 521°C (900° to 970°F) and a contact time of 1 to 3 seconds. The low conversion operation yields high quantities of LCO, some gasoline and not much LPG. The LCO can be recovered from the main column 100. The gasoline fraction can be fed to the secondary reactor at low severity 482° to 521°C (900 to 970°F) and low WHSV, 0.1 to 5 hr$^{-1}$, so the gasoline reforms to convert olefins to aromatics and isoparaffins to upgrade the gasoline quality.

## EXAMPLES

## EXAMPLE 1

[0046]    A fraction of gasoline from an FCC reactor effluent having the properties in Table I was subjected to coked USY zeolite catalyst with 1 to 1.5 wt-% rare earth in a reactor at the conditions in Table I. The reaction yielded a product with the properties in Table I.

TABLE I

| FEED PROPERTIES | |
|---|---|
| IBP, °C (°F) | 121 (250) |
| Aromatics, wt-% | 61.8 |
| Olefins, wt-% | 14.2 |
| Paraffins/Naphthenes, wt-% | 24 |
| RON | 93.3 |
| MON | 81.9 |
| **REACTOR CONDITIONS** | |
| WHSV, $hr^{-1}$ | 1 |
| Reaction Temperature, °C (°F) | 454 (850) |
| Catalyst-to-Oil Ratio | 6.0 |
| Pressure, kPa (psig) | 69 (10) |
| **PRODUCT PROPERTIES** | |
| $C_2^-$, wt-% | 0.6 |
| $C_3$, wt-% | 1.2 |
| $C_4$, wt-% | 2.0 |
| $C_5^+$ / 232°C (450°F), wt-% | 89.4 |
| LCO, wt-% | 4.7 |
| CO, wt-% | 2.1 |
| Gasoline RON | 95.8 |
| Gasoline MON | 84 |
| Aromatics, wt-% | 70 |
| Olefins, wt-% | 1 |
| Paraffins/Naphthenes, wt-% | 29 |

In this example, the olefin concentration dropped from 14.2% to 1 wt-% as a result of the secondary reaction. Whereas, the aromatics concentration increased from 61.8 to 70 wt-%. Additionally, both the RON and the MON increased. The relatively small concentrations of $C_4$ and smaller hydrocarbons reveal that cracking reactions were

5    minor compared to the reformulating, hydrogen transfer reactions indicated by the increase in aromatics.

EXAMPLE 2

[0047]     A separate study was performed to determine the effect on product

properties of four sets of operating conditions on full range FCC gasoline as shown in

Table II.

<div align="center">TABLE II</div>

| FEED PROPERTIES | | | | |
|---|---|---|---|---|
| IBP, °C (°F) | 35 (95) | | | |
| Paraffins, wt-% | 27 | | | |
| Olefins, wt-% | 51 | | | |
| Naphthenes, wt-% | 6 | | | |
| Aromatics, wt-% | 14 | | | |
| $C_4$, wt-% | 2.3 | | | |
| Feed Boiling Over 221°C (430°F), wt-% | 1.3 | | | |
| PROCESS CONDITIONS | A | B | C | D |
| Reaction Temperature, °C (°F) | 399 (750) | 399 (750) | 454 (850) | 482 (900) |
| Catalyst-to-Oil Ratio | 3 | 5 | 5.1 | 5.1 |
| PRODUCT YIELDS, wt-% | | | | |
| $C_2^-$ | 0.06 | 0.13 | 0.43 | 0.60 |
| $C_3$ | 0.82 | 1.22 | 2.85 | 4.16 |
| $C_4$ | 3.5 | 4.53 | 6.75 | 8.35 |
| $C_5^+$ / 220°C (429°F) | 91.3 | 86.4 | 83.1 | 80.0 |
| LCO | 2.5 | 3.69 | 3.28 | 2.87 |
| CO | 0.2 | 1.5 | 1.4 | 1.9 |
| Coke | 1.6 | 2.5 | 2.2 | 2.1 |
| Gasoline Recovery | 94.9 | 90.0 | 86.7 | 83.6 |
| Paraffins | 42 | 47 | 48 | 44 |
| Olefins | 31 | 21 | 18 | 13 |
| Naphthenes | 8 | 8 | 7 | 7 |
| Aromatics | 21 | 23 | 27 | 36 |

As the temperature is increased, the gasoline recovery diminished while the aromatics concentration increased and the olefins concentration decreased. Additionally, cracking as indicated by the amount of $C_4$ and lower carbon number concentration increases as

the reaction temperature and/or catalyst-to-oil ratio increases. Accordingly, the reaction conditions can be tailored to obtain a desired product quality.

EXAMPLE 3

[0048]    The feed in the next set of experiments had the properties given in Table III.

TABLE III

| | |
|---|---|
| Paraffins, wt-% | 28.1 |
| Olefins, wt-% | 50.4 |
| Naphthenes, wt-% | 5.9 |
| Aromatics, wt-% | 14.4 |
| $C_{12}$ Non-Aromatics, wt-% | 1.32 |
| RON | 91.0 |
| MON | 79.3 |
| Road Octane Number | 85.2 |
| Sulfur, ppm | 136 |
| Nitrogen, ppm | 46 |
| $C_4$, wt-% | 2.3 |
| 221°C (430°F) plus, wt-% | 1.3 |
| IBP, °C (°F) | 35    (95) |
| T10 | 51    (123) |
| T30 | 67    (153) |
| T50 | 88    (190) |
| T70 | 118    (244) |
| T90 | 152    (306) |
| EP, °C (°F) | 179    (354) |

5    The foregoing feed was reacted under three different sets of conditions with corresponding product yields and quality given in Table IV.

TABLE IV

| PROCESS CONDITIONS | Run | | |
|---|---|---|---|
| | A | B | C |
| Reactor Temperature, °C (°F) | 427 (800) | 454 (850) | 482 (900) |
| Catalyst-to-Oil Ratio | 6.5 | 6.1 | 5.9 |
| Hydrocarbon Partial Pressure, kPa (psia) | 117 (17.0) | 114 (16.5) | 122 (17.7) |
| System Pressure, kPa (psig) | 278 (40.3) | 276 (40.0) | 273 (39.6) |
| LHSV, hr$^{-1}$ | 4.6 | 4.6 | 4.6 |
| PRODUCT YIELDS, wt-% | | | |
| Dry Gas | 0.4 | 0.7 | 1.1 |
| $C_3$'s | 1.6 | 2.4 | 3.4 |
| $C_4$'s | 6.1 | 7.8 | 9.4 |
| $C_5^+$ Gasoline | 85.5 | 83.0 | 80.0 |
| Paraffins | 53.3 | 54.7 | 52.3 |
| Olefins | 13.8 | 12.4 | 12.3 |
| Naphthenes | 8.1 | 5.5 | 6.2 |
| Aromatics | 24.8 | 27.4 | 29.2 |
| Sulfur, ppm | 69 | 62 | 68 |
| Nitrogen, ppm | 1 | 2 | 4 |
| RON | 87.4 | 88.4 | 90.4 |
| MON | 80.5 | 81.5 | 81.8 |
| Road Octane Number | 84.0 | 85.0 | 86.1 |

The foregoing qualities and yields pertaining to the $C_5^+$ gasoline have been adjusted to reflect the fact that $C_4$'s were present in the feed which did not participate in the reaction and would not be present in the feed to the secondary reactor. Moreover, the data indicates that not much cracking occurred in the reaction because relatively small quantities of $C_4^-$ material is generated. The process also reduces the olefin

106287                                   - 32 -

concentration while increasing the paraffin and aromatics concentration, all without substantial change in the Road Octane Number.

[0049]    Table V gives the breakdown of the product composition from foregoing Run B by carbon number and compound type. The number that is not in parentheses in Table V is the weight percentage of that compound in the feed. Whereas, the number in parentheses is the weight percentage of the compound in the product.

TABLE V

Gasoline Composition
Full Range Feed vs. Product

| Carbon # | Total | Naphthenes | Isoparaffins | n-Paraffins | Cyclic-Olefins | Iso-Olefins | n-Olefins | Aromatics |
|---|---|---|---|---|---|---|---|---|
| 5 | 24.93 (25.32) | 0.1 (0.0) | 7.33 (17.48) | 1.53 (2.49) | 0.61 (0.14) | 8.24 (3.17) | 7.12 (2.03) | --- (---) |
| 6 | 23.00 (23.92) | 1.22 (1.79) | 6.31 (15.28) | 0.92 (1.63) | 2.04 (0.32) | 7.33 (3.12) | 4.68 (1.11) | 0.51 (0.67) |
| 7 | 18.17 (16.43) | 1.79 (1.94) | 3.87 (7.59) | 0.51 (0.90) | 2.24 (0.29) | 4.88 (1.33) | 2.54 (0.29) | 2.34 (4.10) |
| 8 | 14.96 (14.41) | 1.53 (0.87) | 2.54 (3.88) | 0.51 (0.63) | 1.02 (---) | 3.15 (0.46) | 1.32 (---) | 4.88 (8.57) |
| 9 | 12.72 (17.58) | 0.92 (0.64) | 1.83 (2.31) | 0.41 (0.43) | 0.31 (---) | 1.83 (0.16) | 0.81 (---) | A9+ |
| 10 | 3.47 (1.79) | 0.32 (0.24) | 1.12 (1.10) | 0.41 (0.46) | 0.00 (---) | 1.12 (---) | 0.51 (---) | 6.61 (14.04) |
| 11 | 1.42 (0.52) | --- (---) | 0.51 (0.54) | 0.31 (0.00) | 0.00 (---) | 0.41 (---) | 0.2 (---) | |
| Total | 98.68 (100) | 5.87 (5.49) | 23.51(48.19) | 4.58 (6.55) | 6.21 (0.74) | 26.97(8.23) | 17.2 (3.42) | 14.35(27.37) |
| 12 | $C_{12}^+$ Non-Aromatics: 1.3 | | | | | | | |

106287

With regard to Table V, aromatics with nine or more carbon numbers are grouped together. Therefore, the numbers given for carbon numbers 10 and 11 in the "Total" column include only non-aromatic $C_{10}$'s and $C_{11}$'s. The minimal changes in total concentration of each carbon number fraction, especially in the $C_5$-$C_8$ range shows that reformulating hydrogen transfers are predominant over cracking reactions under this set of conditions. Moreover, the large increase in isoparaffins compared to the moderate increase in paraffins greatly offsets the octane value debit resulting from olefin reduction.